and to the solution an excess of methanolic HCl was added. Removing of the solvent *in vacuo* gave the crude amine hydrochloride.

2. **Treatment with Activated Hydrogen.** A suspension of 0.001 mol of the complex and a little amount of 10% palladium on carbon in 10 ml of tetrahydrofuran was shaken in a hydrogenation apparatus at 20 psi. The reaction was stopped when hydrogen absorption ceased (generally after about 1.5 hr). The crude amine hydrochloride was isolated as above.

3. **Treatment with Sodium Borohydride in the Presence of Elemental Sulfur.** When the above-described reduction was applied to a cyclooctadiene or a norbornadiene derivative a mixture of several amines was obtained, owing to the fission of the higher amine that the reduction should have afforded. This inconvenience could be overcome by following procedure 1, except that a small amount of sulfur was added. In this condition the higher amine was the main product of the reduction.

Degradation of Complex IIb by Hydrolysis and Treatment with Cyanide. Complex IIb (2.0 g) was boiled with 10 ml of 37% HCl until a yellow solution was obtained. After cooling and filtering the solution was concentrated *in vacuo*. The residue was suspended in 2 ml of water and excess sodium cyanide was added. The solution was extracted twice with ether and after washing with water, the ethereal solution was acidified with methanolic HCl. Concentration *in vacuo* gave the crude amine hydrochloride.

An absorption band (1.640 cm^{-1}) of this product indicated that an unsaturated bond was present. This material was hydrogenated with hydrogen activated on Raney nickel before gas chromatographic analysis.

General Procedure of Amine Identification. The crude hydrochloride obtained by reductive degradation of the complexes was dissolved in a minimum amount of water, and after addition of excess sodium hydroxide, the free amine was extracted with a known amount of ether. Glpc analysis was carried out both on this solution and an ether solution containing the authentic sample. Peak areas were measured by means of a planimeter.

Acknowledgments. We wish to thank Dr. G. Fontana for his helpful experimental assistance. This work was performed with the financial support of the Italian Consiglio Nazionale delle Ricerche (CNR).

Addition Reactions on Coordinated Olefinic Ligands. II. The Reaction between Amines and Monoolefins Coordinated in *cis*-Dichloro(olefin)(*t*-phosphine)platinum(II) Complexes

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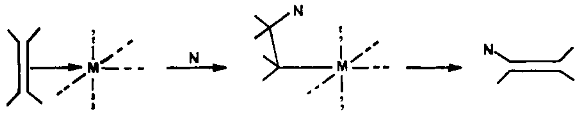
Abstract: Treatment with amines of olefin complexes of the type *cis*-$PtCl_2(Ol)(PR_3)$, in which Ol = ethylene, propene, and 1-butene and R = *n*-butyl and phenyl, led to isolable carbon–platinum σ-bonded derivatives. Dimethyl-, diethyl-, and dibutylamines were mainly used as the attacking nucleophiles. The behavior of ammonia, ethylamine, and triethylamine in the attack was also examined. The addition of the amine to the coordinated double bond was proved by degradative studies. Data on the stereochemistry of the addition of secondary amines to the tri-*n*-butylphosphine complexes were obtained.

The formation of stable alkyl derivatives of transition metals has been related[1] to the energy gap between the highest energy occupied orbital and the lowest energy vacant one associated with the metal. On this basis it is possible to explain why the stability of platinum(II) and palladium(II) alkyls depends on the presence of π-bonding ligands.[2] The role played by such ligands involves the modification of the energy of non-σ-bonding orbitals which increases the cited energy gap. As shown in reaction scheme A a σ-bonded derivative is assumed to be the intermediate in the reaction between a nucleophile, N, and a coordinated monoolefin. In the absence of π-bonding ligands such a compound should not be stable. In fact only a vinyl monomer is generally isolated,[3] according to the last step of reaction scheme A. On the other hand many other metals, or even Pt(IV), form stable alkyl derivatives but do not form stable olefin π complexes. For example, no stable π complexes are known to form by interaction of mercury salts with olefins, the alkyl derivatives being the isolable reaction products.[4] A known case in the transition-metal chemistry in which the first step of eq A is an actual process and both the starting olefin π complex and the alkyl derivative are sufficiently stable and isolable is the one involving the attack of a hydride to an olefin coordinated in a metal carbonyl.[5] It must be pointed out that analogous reactions, which are known to occur with related compounds, show substantial differences. Typical examples are the addition of nucleophiles to one of the two double bonds of a coordinated diene which leads to stable σ-bonded derivatives,[6] and the halogen addition[7] to the double



(A)

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(1) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705, 4020 (1959).

(2) The subject has been reviewed by R. J. Cross, *Organometal. Chem. Rev.*, 2, 97 (1967).

(3) A. Aguilo, *Advan. Organometal. Chem.*, 5, 321 (1967).

(4) However, stable intramolecular mercury–arene π coordination has been already reported: E. F. Kiefer, W. L. Waters, and D. A. Carlson, *J. Am. Chem. Soc.*, 90, 5127 (1968).

(5) M. L. H. Green, A. G. Massey, J. T. Moelwyn-Hughes, and P. L. I. Nagy, *J. Organometal. Chem.* (Amsterdam), 8, 511 (1967), and references cited therein.

(6) See note I, R. Palumbo, *et al.*, *J. Am. Chem. Soc.*, 91, 3874 (1969), and pertinent references cited therein.

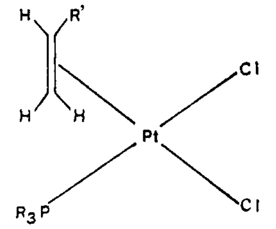
(7) M. A. Bennet, J. Chatt, G. J. Erskine, J. Lewis, R. F. Long, and R. S. Nyholm, *J. Chem. Soc.*, *A*, 501 (1967).

bond of an unsaturated tertiary arsine coordinated to platinum(II), which gives stable alkyl derivatives of platinum(IV).

Previous studies[6] on the addition of nucleophiles on diene complexes have already shown that aliphatic amines are very effective in the attack to a coordinate diene. The addition of amines to simple coordinated olefins was then examined.[8] In this paper results on the addition of amines to *cis*-dichloro(olefin)(*t*-phosphine)-platinum(II) complexes, chosen on the ground of the quoted stability requirements, are reported.

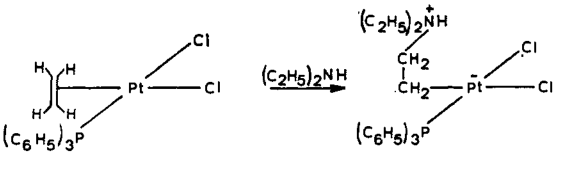
Results

Alkyl Formation. Reactions of *cis*-dichloro(olefin)-(tri-*n*-butylphosphine)platinum(II) (olefin = ethylene, propene, and 1-butene) and of *cis*-dichloro(ethylene)-(triphenylphosphine)platinum(II) were examined. The propene and the 1-butene complexes were obtained by exchange of the ethylene compound with the higher olefins. Complex I was synthetized following a procedure similar to the one described[9] for the known tri-*n*-butylphosphine complex.



I	$R = C_6H_5$	$R' = H$
IIa	$R = n\text{-}C_4H_9$	$R' = H$
IIb	$R = n\text{-}C_4H_9$	$R' = CH_3$
IIc	$R = n\text{-}C_4H_9$	$R' = C_2H_5$

Dimethyl-, diethyl-, and dibutylamines were mainly used as the nucleophilic agents. Reactions with NH_3 and other substituted aliphatic amines were shortly examined. Equation B illustrates the reaction of complex I with diethylamine. The reaction was carried out by adding dropwise in the cold (0°) a methylene chloride solution of the amine to a solution of the complex in the same solvent. A simple reaction pattern of the type represented by eq B is valid only for secondary or tertiary amine addition. Accordingly, upon attack of triethylamine on the ethylene complexes I and IIa, the totally alkylated ammonium derivative was formed, as was shown by hydrolysis of the complexes.

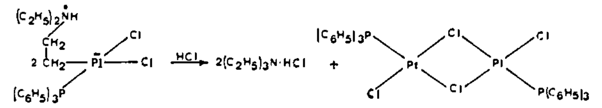


(B)

When ammonia reacted with the ethylene complexes I and IIa the reaction did not stop to the first step but consecutive alkylation occurred. Actually, on acid hydrolysis (as described below) of the crude reaction product, mono-, di-, and triethylamines were formed. Similarly, the hydrolysis of derivatives formed upon addition of ethylamine to I and IIa yielded both di- and triethylamines.

Molecular Structure of the Alkyl Species. Only the two alkyl derivatives obtained from the ethylene complexes I and IIa upon addition of diethylamine were recrystallized. Analyses were in agreement with the stoichiometry corresponding to the formulation of eq B.

Evidence of the amine addition to the coordinated double bond was obtained by the chemical behavior of the addition products in degradation reactions. Hydrochloric acid has been described[1] to cleave the carbon–platinum σ bond quantitatively in anhydrous media, yielding the saturated hydrocarbon corresponding to the alkyl group. We found that the hydrolysis could be obtained by stirring the complex with 37% aqueous HCl at room temperature. In all cases, but for the recrystallized derivatives of the ethylene complexes, the reaction was carried out on the crude addition product. Upon hydrolysis this material gave the binuclear halogen-bridged *t*-phosphine complex and the amine resulting from the addition to the olefin, *i.e.*, an N-alkylated derivative of the attacking amine. The following equation illustrates the process for the diethylamine derivative reported in eq B. The N-alkylated amine can also be isolated by destructive reduction of the alkyl derivative with $NaBH_4$ in THF.



(C)

We note that potassium cyanide treatment of the derivatives obtained from the complexes I and IIa upon attack of diethylamine did not lead to the formation of free triethylamine, but only diethylamine was formed. Besides, the spectral (uv, visible, and nmr) properties of an authentic sample of *trans*-dichloro(triphenylphosphine)triethylamineplatinum(II) prepared by a procedure similar to the one described[10] for the analogous *p*-toluidine complex were largely different from the properties of the diethylamine derivative obtained from I. These observations rule out the possibility that the higher amine is formed *before* the treatment with HCl, because of a poor stability of the alkyl derivative. In the latter case no hydrolysis would be involved but only displacement of the N-alkylated amine coordinated in the reaction product.

The nmr spectrum of the complex I is characterized by a complex multiplet centered approximately at δ 7.65 and a triplet at 4.05, which is assigned to the ethylene molecule π coordinated to the platinum atom. The intensities of the three bands assigned to the ethylene protons are in the ratio expected because of the presence of ^{195}Pt nuclei (33% natural abundance) which possess a spin of $^1/_2$. The coupling $^2J_{^{195}Pt-CH_2}$ has a magnitude of 60 Hz. The nmr spectrum of the alkyl derivative obtained upon addition of diethylamine to the complex I was recorded at 0° and shows a disappearance of the resonance lines due to the ethylene group π coordinated to the platinum atom. Two multiplets appear in the spectrum in the regions between δ 2.2 and 3.3 and between δ 0.8 and 1.7. These multiplets are assigned to the methyl and methylene groups of the two ethyl substituents, which overlap considerably with the resonances (shifted upfield) of the methylene groups deriving from the ethylene molecule. No precise assignment was made because of the complexity of the aliphatic region of the spectrum.

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[8] For a short preliminary account see: G. Paiaro, A. De Renzi, A. Panunzi, and R. Palumbo, *Chim. Ind.* (Milan), 50, 924 (1968).

[9] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1662 (1964).

[10] R. J. Goodfellow and L. M. Venanzi, *ibid.*, 7533 (1965).

Table I. Higher Amines from the Hydrolysis of the Addition Products[a]

Olefin complex	Amine used in the attack		
	$(CH_3)_2NH$	$(C_2H_5)_2NH$	$(C_4H_9)_2NH$
IIa	$C_2H_5N(CH_3)_2$, 68%	$(C_2H_5)_3N$, 62%	$C_2H_5N(C_4H_9)_2$, 55%
IIb	$(CH_3)_2CHN(CH_3)_2$, 47%	$(CH_3)_2CHN(C_2H_5)_2$, 45%	$(CH_3)_2CHN(C_4H_9)_2$, 38%
IIc		$CH_3(CH_2)_2CH_2N(C_2H_5)_2$, 20% $CH_3(C_2H_5)CHN(C_2H_5)_2$, 17%	$(n\text{-}C_4H_9)_3N$, 16% $CH_3(C_2H_5)CHN(C_4H_9)_2$, 14%

[a] Yields are calculated on the starting π complex.

The infrared spectrum of the latter compound shows no absorption in the 1500–1520-cm^{-1} region, where C=C stretching modified by coordination is generally reported to appear. The infrared spectrum of the starting ethylene π complex shows the corresponding band at 1515 cm^{-1}. Furthermore, in the spectrum of the alkyl derivative no absorption bands in the 3200–3220-cm^{-1} region, which are characteristic[11] of the NH stretching of a platinum(II)-coordinated secondary amine, were observed. Finally, we note that no band in the 2000–2200-cm^{-1} region which could be assigned to the Pt–H stretching was detected.

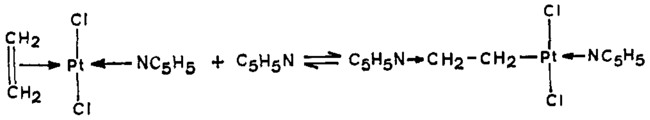
Stereochemistry of the Addition. The more reliable set of data on the stereochemistry of the addition was derived from the derivatives obtained by reaction of the π complexes with secondary amines. Actually, as mentioned previously, in the case of ammonia or ethylamine the tendency to consecutive alkylations can lead to mixtures of different amines. In the case of propylene or 1-butene, in which two nonequivalent sites of addition are present, these mixtures are so complicated that no detailed analysis was actually feasible.

In Table I the amines obtained by the destructive reduction of the derivatives formed from the complexes IIa, IIb, and IIc on addition of dimethyl-, diethyl-, and dibutylamines are reported. Yields are calculated on the starting olefin complex for sake of homogeneity, some alkyl derivatives (as noted before) having not been crystallized. An important steric feature of the attack is that the hindrance of the alkyl substituent of the coordinated ethylene is responsible for the attack direction more than the hindrance of the alkyl substituents of the amine. No *normal* propyl derivatives were obtained from the propene complex within the accuracy of the gas chromatographic determinations.

The results can be preliminarily compared with those relative to the amine attack to diene complexes,[6] taking into account that a meaningful conclusion should be postponed after complete elucidation of the reaction mechanism for both systems. It appears however that a Markovnikov type of attack is possible only when sterical factors do not interfere.

Discussion

We notice that our preliminary report was confirmed by a recent pmr study,[12] which gave evidence of alkyl formation from a platinum(II)–ethylene complex in the presence of pyridine according to the equation



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \rightarrow \overset{Cl}{\underset{Cl}{Pt}} \leftarrow NC_5H_5 + C_5H_5N \rightleftharpoons C_5H_5N \rightarrow CH_2-CH_2-\overset{Cl}{\underset{Cl}{Pt}} \leftarrow NC_5H_5$$

It is also worth mentioning that the addition direction found in the case of the propene complex is the same reported by Stern and Spector in a brief note,[13] in which the activity of palladium(II) chloride in the reaction of propene with n-butylamine and acetamide to give the N-isopropyl-substituted nucleophiles has been described. The direction observed in the amine attack on the complexes IIb and IIc should also be compared with that reported for the Wacker process. In that case typical data[14] (in 1 N HCl at 70°; catalyst: 0.05 M K_2PdCl_4) for propene and 1-butene oxidation were: from propene, 15% to the aldehyde, 85% to the ketone; from 1-butene, 10% to the aldehyde, 90% to the ketone.

Only scant data on the mechanism of attack of a nucleophile to a coordinated olefin are available. In particular, meaningful kinetic data[15] on the attack of OH^- to a coordinated ethylene molecule indicate that a four-center *cis* addition is involved. Recently, some general reasons were given[16] in order to explain why this mechanism is expected for addition reactions on monoolefin complexes, whereas a case was reported in which the same stereochemical behavior has been proposed for a diene complex, an octahedral coordination being involved. Because of the importance of the processes involving nucleophilic attack on coordinate monoolefins, the reported amine attack appears of interest as a possible source of more information on many unknown features of the reaction mechanism in these systems. On the other hand, at the present stage of our work, a four-center *cis* addition appears to be a reasonable explanation of the general reaction mechanism also in the case of amine addition.

We wish to present some observations on the successive alkylation of ammonia and a primary amine. It has been found that the tendency to successive alkylation steps is remarkable in the case of ammonia (to a larger extent) and ethylamine addition, and is negligible in the addition products formed after the attack of diethylamine to I and IIa (as well as to IIb and IIc). In fact, no tetraethylammonium ions were found in the degradation products in the latter case. Such behavior could be related to the pK's of the ammonium ions formed upon addition of the amines to the π complexes, supposing that successive alkylation will involve collapse of the less substituted alkyl derivative, with

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(11) (a) R. G. Denning and L. M. Venanzi, *J. Chem. Soc.*, 3241 (1963); (b) D. V. Claridge and L. M. Venanzi, *ibid.*, 3419 (1964).

(12) P. D. Kaplan, P. Schmidt, and M. Orchin, *J. Am. Chem. Soc.*, **90**, 4175 (1968).

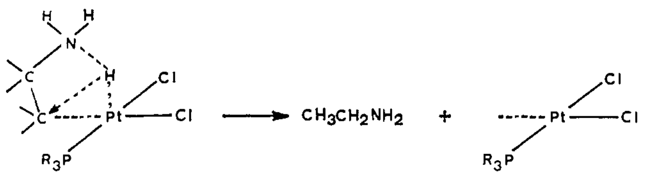
(13) E. W. Stern and M. L. Spector, *Proc. Chem. Soc.*, 370 (1961).

(14) W. Hafner, R. Jira, J. Sedlmeier, and J. Smidt, *Chem. Ber.*, 1575 (1962).

(15) P. M. Henry, *J. Am. Chem. Soc.*, **86**, 3246 (1964).

(16) B. L. Shaw, *Chem. Commun.*, 464 (1968).

migration of a positive hydrogen. The schematic equation represents this type of intramolecular transformation.



The process would involve consecutive steps of bond making and breaking. Assumption is made that a hydrogen atom is bonded to the metal atom (similar types of bonding have been previously described[17]). It seems to us that since increasing alkyl substitution increases the p*K*'s of the ammonium ions, it will consequently increase the stability of the addition products, as has been found. Diethylamine would be, therefore, already sufficient to produce a stable alkyl derivative.

We note finally that a reason of interest for the isolation of alkyl derivatives obtained upon attack of nucleophiles of largely variable steric hindrance and basicity (as the amines) stems from previous results achieved by stereochemical studies[18] on olefin complexes. It is reasonable to expect that the study of nucleophilic attack on the quoted diastereoisomeric π complexes containing prochiral coordinated olefins can shed some light on the stereochemical features of the reactions of olefins in the presence of transition metals.

Experimental Section

In the preparation and isolation procedures, all operations were carried out in nitrogen. Infrared spectra were determined on Nujol and hexachlorobutadiene mulls on a Beckman IR-9 instrument. Molecular weights were determined in chloroform solution with a Hitachi-Perkin-Elmer Model 115 apparatus. Melting points are uncorrected. Gas chromatographic analyses were carried out on a Fractovap GV chromatograph, using a 3-ft column packed with SE 30 on Chromosorb. Some of the elemental analyses were performed in this laboratory and other by Mikroanalytisches Laboratorium of the Max Planck Institut für Köhlenforschung, Mülheim.

Materials. All solvents were distilled through a fractionation column after treatment with a suitable drying agent and stored and handled in nitrogen. The other chemicals used were of Analar grade.

Olefin Complexes. *cis*-Dichloro(ethylene)(tri-*n*-butylphosphine)platinum(II) was prepared according to a known procedure.[9] The corresponding propene and 1-butene complexes were both prepared by exchange of the ethylene complex with the higher olefin. The ethylene complex was dissolved in the minimum amount of methylene chloride in a stopcock side-armed flask equipped with a condenser (cooling medium: Dry Ice–acetone). An excess of the gaseous olefin was admitted through the stopcock and the reaction mixture was allowed to reflux until complete exchange (about 12 hr for the propene complex, 4 hr for the butene complex). After removing the solvent *in vacuo* the crude compounds were recrystallized from methylene chloride–heptane.

cis-Dichloro(propene)(tri-*n*-butylphosphine)platinum(II): white crystals; yield, 92%.

Anal. Calcd for $C_{15}H_{33}PCl_2Pt$: C, 35.3; H, 6.5. Found: C, 34.9; H, 6.4.

cis-Dichloro(1-butene)(tri-*n*-butylphosphine)platinum(II): white crystals; yield, 87%.

Anal. Calcd for $C_{16}H_{35}PCl_2Pt$: C, 36.65; H, 6.7. Found: C, 36.4; H, 6.5.

cis-Dichloro(ethylene)(triphenylphosphine)platinum(II) was prepared by splitting with ethylene the dichloro(triphenylphosphine)platinum(II) dimer, which was obtained according to the method of Smithies, *et al.*[19] A suspension of the binuclear complex (10.55 g, 0.01 mol) in 30 ml of chloroform in a Paar apparatus was shaken with 4 atm of ethylene, until complete dissolution occurred (about 24 hr at room temperature). The solution was filtered and crystallization was obtained upon addition of toluene and successive removal of chloroform *in vacuo*. Recrystallization from chloroform–toluene gave 7.23 g (yield, 65%) of white crystals. The complex, as the previously described propene and 1-butene ones, above 100° lost olefin and appeared to revert to the halogen-bridged binuclear compound, since it turned to a yellow color.

Anal. Calcd for $C_{20}H_{19}PCl_2Pt$: C, 44.15; H, 3.45. Found: C, 43.7; H, 3.2.

Authentic Amine Samples. N,N-Dimethylethylamine and N,N-dimethylisopropylamine were prepared according to the Eschweiler–Clarke procedure as described by Spialter and Pappalardo.[20] The procedure of Caspe[21] was used for the preparation of N,N-dibutylisopropylamine, N,N-diethyl-*n*-butylamine, N,N-diethyl-*sec*-butylamine, N,N-diethylisopropylamine, N,N-dibutylethylamine, and N,N-dibutyl-*sec*-butylamine.

General Procedure for Amine Addition. Equimolar amounts of the amine and of the olefin complexes were allowed to react in each case. The amine was added as 0.2 *M* methylene chloride solution to a stirred ice-cold solution (0.1 *M*) of the complex in the same solvent. After stirring 30 min the solvent was removed at reduced pressure, keeping the reaction mixture at 0°. The crude reaction product was throughly dried *in vacuo* at room temperature.

When ammonia was used in the attack, the gaseous reagent was introduced slowly in the reaction vessel through a serum cap by use of a hypodermic syringe furnished with a stopcock.

Isolation of Pure Alkyl Derivatives. Both derivatives obtained from the addition of diethylamine to the complexes I and IIa were isolated. In the case of complex I solvent removal from the reaction solution was interrupted when the volume was about one-third of the initial volume. Two volumes of acetone were added and the mixture was kept at −10° for about 1 hr. The white precipitate was filtered, washed with acetone, and dried *in vacuo*: yield 60%; mp 134–136° dec. The complex appeared to be stable at room temperature, but decomposed in solution at 40° as the nmr spectra showed.

Anal. Calcd for $C_{24}H_{30}NPCl_2Pt$: C, 45.8; H, 4.8; N, 2.2; mol wt, 629.2. Found: C, 45.5; H, 4.6; N, 2.1; mol wt, 593.

The other derivative was obtained by a similar procedure, yield 43%. The crystallized complex was slightly impure with diethylamine hydrochloride. Satisfactory analyses were obtained after washing with small amounts of methanol.

Anal. Calcd for $C_{18}H_{42}NPCl_2Pt$: C, 37.95; H, 7.45; N, 2.45; mol wt, 569.3. Found: C, 37.5; H, 7.2; N, 2.2; mol wt, 547.

Both the alkyl derivatives gave triethylamine on destructive reduction (yield >95%). By treatment with KCN in aqueous suspension diethylamine (yield >95%) was obtained.

Degradative Studies. 1. Reduction with $NaBH_4$. To a suspension of the crude alkyl derivative (0.5 g) in 10 ml of tetrahydrofuran, an excess of sodium borohydride was added slowly at room temperature with stirring. When stopping the stirring left a clear solution on metal black, the reaction mixture was filtered and to the solution an excess of methanolic HCl was added. Removing the solvent *in vacuo* gave the crude amine hydrochloride.

2. Acid Hydrolysis. A suspension of the crude alkyl derivative (0.5 g) in 20 ml of 37% HCl was stirred at room temperature about 6 hr. After filtering, the aqueous solution was concentrated *in vacuo*, giving the crude amine hydrochloride.

General Procedure of Amine Identification. The crude amine hydrochlorides obtained by degradative procedures were dissolved in a minimum amount of water and, after addition of an excess of sodium hydroxide, the free amine was extracted with a known amount of ether. Glpc analyses were carried out both on this solution and on an ether solution containing the authentic sample. Peak areas were measured by means of a planimeter.

Total yield for the higher amine mixtures obtained from the addition products of ammonia and ethylamine to the complexes I and IIa were about 80%. In the former case mono-, di-, and tri-

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[17] (a) K. Nakamoto, P. I. Mc Carthy, I. Fujita, R. A. Condrate, and G. T. Behnke, *Inorg. Chem.*, **4**, 36 (1965); (b) N. A. Bailey, J. M. Jenkins, R. Mason, and B. L. Shaw, *Chem. Commun.*, 237 (1965).

[18] (a) G. Paiaro and A. Panunzi, *J. Am. Chem. Soc.*, **86**, 5148 (1964); (b) A. Panunzi and G. Paiaro, *ibid.*, **88**, 4843 (1966).

[19] A. C. Smithies, M. Rycheck, and M. Orchin, *J. Organometal. Chem.* (Amsterdam), **12**, 199 (1968).

[20] L. Spialter and J. A. Pappalardo, *J. Org. Chem.*, **22**, 840 (1957).

[21] S. Caspe, *J. Am. Chem. Soc.*, **54**, 4457 (1932).

ethylamines were obtained approximately in the ratio 1:4:6. In the latter case di- and triethylamines were obtained in approximately a 1:1.6 ratio. Total yield from the ammonia or ethylamine derivatives of IIb and IIc ranged from 25 to 10%.

In the case of the derivative obtained by addition of triethylamine to the complex IIa the crude tetraethylammonium hydrochloride obtained by method 2 was dissolved in a small amount of ethanol. To this solution a cold saturated solution of picric acid in ethanol was added. After removal of the solvent *in vacuo*, the dried residue was recrystallized from ethanol–ether. The identification was carried out by comparing the powder pattern of this material with that of an authentic sample.

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Calorimetric Study of the 2,4,6-Tri-*t*-butylphenoxy Radical in Solution

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Abstract: Direct experimental determinations of the differences in the heats of formation in solution of a free radical and its hydrogenated precursor have been carried out for the first time. The method consists of calorimetric measurements of the heat of the quantitative reaction of hydrazobenzene with 2,4,6-tri-*t*-butylphenoxy radical (I) to produce *trans*-azobenzene and 2,4,6-tri-*t*-butylphenol (II). Values of $(\Delta H_f)_{II^s} - (\Delta H_f)_{I^s}$ calculated from these studies vary from 28.13 ± 0.13 kcal/mol in pure carbon tetrachloride to 29.73 ± 0.07 kcal/mol in the mixed solvent carbon tetrachloride–dioxane (mole fraction 0.53). Calorimetric studies of the reaction of 4-*t*-butylphenol with I to produce II and 4-(4-*t*-butylphenoxy)-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene-1-one (IV) were also carried out in a number of solvents and the results of those studies are internally consistent with the results of the hydrazobenzene reaction. A comparison of the solution properties of I with those of 1,3,5-tri-*t*-butylbenzene (V) reveals that specific solvent interactions with the radical due to its free electron are small (±0.5 kcal/mol) and thus V is a good model for I in solution. The difference in the heats of formation of a number of other stable free radicals, B·, and the molecules from which they are formed, BH, is then calculated by combining the results of the present study and the results of earlier studies of the reactions of I with BH to produce II and B·. The strain energy in II associated with steric interaction of 2,6-di-*t*-butylphenol group is calculated in the gas phase as equal to 8.0 ± 2.0 kcal/mol. The manifestations of this strain energy in the phenomena of the synergistic behavior of mixtures of hindered and nonhindered phenols as antioxidants and the ease of disassociation of dimers derived from 2,5-di-*t*-butylphenoxy radicals are then discussed.

The values of the bond energies of organic molecules and the heats of formation of the free radicals and atoms derived from them are of considerable theoretical and practical interest. Determinations of such quantities have been limited exclusively to the gas phase since the conventional techniques are based upon either the pyrolysis of the parent molecule or the thermal formation of atoms from a diatomic molecule such as I_2.[1] Among the limitations of these gas-phase techniques are (1) they are confined to systems where the reactants and products are of moderately low molecular weight, and (2) the parent molecule must not contain bonds which are less thermally stable at elevated temperatures than the bond whose energy is to be determined. For these reasons the development of techniques for the determination of the heats of formation of free radicals at moderately low temperatures, *i.e.*, in the liquid phase where such limitations may be circumvented, would be very desirable.

In contrast to most free radicals, solutions of the 2,4,-6-tri-*t*-butylphenoxy radical (I) may be prepared and these solutions are stable in the absence of oxygen and other reactive compounds. As a result of this unique property a classical approach to the heat of formation of I may be taken, *i.e.*, the heat of its reaction can be directly measured in systems for which the heats of formation of the other reactants and products are known or may be determined. Since I engages in reversible hydrogen atom transfer reactions with many reactive organic compounds, *i.e.*, hydroperoxides[2] and phenols,[3] to form 2,4,6-tri-*t*-butylphenol (II) and the corresponding oxy radical, the heats of formation of a variety of free radicals not amenable to study by the usual gas-phase techniques may be determined if the difference in the heats of formation of I and II is known.

The present work describes the direct calorimetric determination of the differences in the heats of formation of I and II in a variety of solvents. A combination of the results of this study with the results of earlier equilibrium studies of I and II with other stable free radicals has led to values of the difference in the heats of formation in solution of a number of these free radicals and their hydrogenated precursors. In addition a quantitative estimate of the strain energy present in II has been obtained and its significance in the chemical reactions of II has been analyzed.

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